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Distribution Coefficients for Radionuclides in Aquatic Environments

Effects of Dissolved Organic Compounds on the Distribution Coefficients of ^{57}Co, ^{106}Ru, ^{137}Cs, and ^{241}Am

Prepared by J. R. Clayton, Jr., T. H. Sibley, W. R. Schell

College of Fisheries
University of Washington

Prepared for
U.S. Nuclear Regulatory
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LIST OF PREVIOUS REPORTS

Distribution Coefficients for Radionuclides in Aquatic Environments. I. Development of Methods and Results for Plutonium and Americium in Fresh and Marine Water-Sediment Systems. Annual Report: August 1976 - July 1977. A. H. Seymour, A. Nevissi, W. R. Schell, and A. Sanchez. NUREG/CR-0801. 38 pp.

Distribution Coefficients for Radionuclides in Aquatic Environments. II. Studies in Marine and Freshwater Sediments Systems Including the Radionuclides ^{106}Ru, ^{137}Cs, and ^{241}Am. Annual Report: August 1977 - July 1978. W. R. Schell, T. H. Sibley, A. Nevissi, and A. Sanchez. NUREG/CR-0802. 70 pp.

Distribution Coefficients for Radionuclides in Aquatic Environments. III. Adsorption and Desorption Studies of ^{106}Ru, ^{137}Cs, ^{241}Am, ^{85}Sr, and ^{237}Pu in Marine and Freshwater Systems. Annual Report: August 1978 - July 1979. W. R. Schell, A. L. Sanchez, T. H. Sibley, and J. R. Clayton, Jr. NUREG/CR-0803. 76 pp.

Distribution Coefficients for Radionuclides in Aquatic Environments. Methodology. W. R. Schell, A. Sanchez, T. H. Sibley, A. E. Nevissi, J. R. Clayton, Jr., and E. A. Wurtz. NUREG/CR-1852, Vol. 1. 27 pp.

Distribution Coefficients for Radionuclides in Aquatic Environments. Adsorption and Desorption Studies of ^{137}Cs. W. R. Schell, A. L. Sanchez, and T. H. Sibley. NUREG/CR-1852, Vol. 2. 49 pp.

Distribution Coefficients for Radionuclides in Aquatic Environments. Adsorption and Desorption Studies of ^{85}Sr, W. R. Schell, A. L. Sanchez, and T. H. Sibley. NUREG/CR-1852, Vol. 4. 35 pp.

Distribution Coefficients for Radionuclides in Aquatic Environments. Adsorption and Desorption Studies with ^{244}Cm. E. A. Wurtz, T. H. Sibley, and W. R. Schell. NUREG/CR-1852, Vol. 7. 21 pp.

Distribution Coefficients for Radionuclides in Aquatic Environments. Dialysis Experiments in Marine Environments. T. H. Sibley, A. E. Nevissi, and W. R. Schell. NUREG/CR-1853, Vol. 2. 51 pp.

ABSTRACT

Organic compounds have the capacity to alter the partitioning between particulate and soluble phases of certain radionuclides in sediment-water systems from natural environments. We studied the effects of a variety of selected organic compounds upon sediment-water distribution coefficients for four radionuclides--^{57}Co, ^{106}Ru, ^{137}Cs, and ^{241}Am. Natural sediment-water samples from lake, river, and estuarine environments were used in these studies. The results show that organic compounds can significantly change the distributions of some radionuclides between water and sediment, although other environmental factors must be considered in association with the organic compounds.

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EFFECTS OF DISSOLVED ORGANIC COMPOUNDS ON THE DISTRIBUTION COEFFICIENTS OF ^{57}Co, ^{106}Ru, ^{137}Cs, AND ^{241}Am

1.0 INTRODUCTION

In an effort to understand and assess the potential problems of radionuclides in aquatic ecosystems, numerous studies have been conducted to describe the environmental distributions of several different nuclides. A major limitation of these data is that the physical, chemical, and biological mechanisms actually producing the observed distributions have seldom been investigated. Such information is essential for successfully understanding and predicting the environmental fates and biological availabilities of radionuclides.

One approach to the problem of defining the behavior of many radionuclides in aquatic systems utilizes the fact that their ultimate distributions and fates can be influenced significantly by associations with in situ sediments and/or suspended articles (Duursma and Gross 1971). Such associations can be quantitatively described by the partition coefficient between sediment and water, the distribution coefficient, K_d*. Distribution coefficients for a given radionuclides may be influenced by system variables such as salinity, temperature, hydrogen ion concentration (pH), concentration and surface charcteristics of the sediment or suspended particles and specific chemical composition of the aqueous medium. Some of these parameters and their possible effects on K_d values have been considered in other reports in this series. This report presents information we have obtained to evaluate the effects of organic compounds on K_d values.

1.1 Background

Organic compounds occurring in natural water systems have the potential to affect the aquatic distribution and fate of radionuclides. Although studies attempting to look at natural organic compound-radionuclide interactions are scarce, a considerable body of information exists regarding associations of organic compounds with stable metallic elements. Chemical processes governing the interactions with organic compounds should be similar for both stable elements and radionuclides since they share common chemical properties. Therefore, background information pertaining to organo-metallic associations is relevant to this report.

---

*$K_d = \frac{\text{quantity (activity) of radionuclide/g of sediment or particles}}{\text{quantity (activity) of radionuclide/ml of ambient water}}$

Recent interest in natural organo-metallic interactions is due in large part to two types of observations: 1) concentrations of certain stable elements in natural water systems have been noted to be considerably higher than would be predicted from solubility products of the least soluble inorganic species of these elements (Presley et al. 1972; Siegel 1971), and 2) productivity of aquatic biota can be significantly affected by in situ organic chelating agents (Barber 1973; Gnassia-Barelli et al. 1978; Huntsman and Barber 1975; Steeman-Nielsen and Wium-Andersen 1970).

A number of studies have attempted to isolate and identify the metal complexing fractions of organic matter in natural water and sediment systems. For example, metal complexing capacities have been determined for 1) different molecular weight fractions of naturally-occurring organic matter (Means et al. 1977; Ramamoorthy and Kushner 1975; Schindler et al. 1972), and 2) isolates of humic acid compounds (Mantoura et al. 1978; Nissenbaum and Swaine 1976; Rashid 1971). A major limitation in all of these studies is the fact that the exact chemical identity of these natural organic compounds remains unknown.

An alternative approach taken in a number of studies to assess the potential influences of organic compounds on the aquatic behavior of various metals and/or radionuclides has involved the addition of specific organic compounds to test systems (Davis and Leckie 1978a and b; Rashid and Leonard 1973; Vuceta and Morgan 1978). Although the environmental relevance of some of these organic compounds may be questionable, the data involved do show that organic compounds can have dramatic effects. For example, certain compounds can either 1) increase the apparent solubility of various elements due to the formation of soluble organo-metallic complexes, or 2) enhance the tendencies for elements to associate with available particulate phases. The latter phenomenon can be explained by the association of the organic compounds in question with both the metals and the available particulate matter. As emphasized in these references, the ultimate disposition of a given organo-metallic association in a particular sediment-water system will depend upon factors such as the chemistry of the individual metal (or radionuclide), the concentration of other metals and the concentration of other organic and inorganic complexing agents. In summary, organic compounds have the potential to significantly affect the environmental distributions and fates of many radionuclides, but their actual effect will depend upon interactions among other environmental conditions which may be site-specific.

1.2 Objectives

The general objective for this program is to obtain information for predicting the fate of radionuclides that may be released from nuclear power plants or waste storage facilities into aquatic environments.

In particular, these studies are intended to obtain information on the accumulation of radionuclides by suspended particulate matter. These data will contribute important parameters for modeling the hydrological transport of radionuclides in marine, estuarine, and freshwater environments. Such models can be used to predict the eventual environmental distributions of radionuclides following a release.

This report will describe the effects of specific organic compounds on the distribution coefficients of ^{57}Co, ^{106}Ru, ^{137}Cs, and ^{241}Am in freshwater and marine sediment-water systems.

2.0 METHODS AND MATERIALS

The effects of a variety of organic compounds upon sediment-water distribution coefficients (K_d) were determined for four radionuclides--^{57}Co, ^{106}Ru, ^{137}Cs, and ^{241}Am. The organic compounds tested were acetic acid, salicylic acid, 1-nitroso-2-naphthol, 1,10-phenanthroline, EDTA, glycolic acid, and humic acids. The humic acids used in these studies were purchased from Aldrich Chemical Company. The above organic compounds were chosen primarily for the variety of functional groups available for interactions with both the radionuclides and the suspended sediment particles. The latter two compounds, however, may have particular environmental relevance. Glycolic acid is a major natural excretory product of aquatic flora (Hellebust 1974). Humic acids are compounds derived from organic precursor molecules by biogeochemical processes which normally constitute an important fraction of the organic matter found in natural aquatic systems (Head 1976; Khaylov 1968; Nissenbaum and Kaplan 1972).

Sediments and water samples used in these experiments were obtained from three locations--Lake Washington (freshwater), the mouth of Cattaraugus Creek entering Lake Erie (freshwater), and three stations in the Hudson River (estuarine). All water used in the experiments was filter-sterilized by passage through 0.22 μm Nucleopore polycarbonate membrane filters or 0.30 μm Millipore membrane filters. Sediments which passed through a 0.063 mm geological sieve, less than 63 μm size fraction, were used for the experiments.

Adsorption K_d values were determined using a constant shaking technique similar to that of Duursma and Bosch (1970) and Murray and Murray (1973). Briefly, the method was the following:

1) Measured quantities of the radionuclides, a stock sediment suspension and a stock organic compound solution were added to a known volume of the appropriate water sample. The pH values of the resulting solutions were then readjusted to the initial values of the natural water samples with NaOH and/or HCl. The resulting radionuclide concentrations in all experiments were between 2-46 x 10^{-11} Ci/ml solution for each radionuclide. Sediment concentrations were either 40 mg/l or 200 mg/l.

2) The experimental sediment-water solution was shaken at 200 rpm in a constant temperature (4-8°C) room.

3) Subsamples were collected at designated time intervals during an experiment and filtered to obtain separate particulate and dissolved radionuclide fractions.

Measurements of pH were made at each sampling time. The concentrations of radionuclide on the filter and in the filtrate were subsequently measured with a Ge(Li) detector and K_d values calculated.

To minimize the effect of unwanted microorganisms upon experimental results several sterilization methods were employed. As already mentioned, all water was initially filter-sterilized. In studies using Lake Washington and Cattaraugus Creek sediments and waters all experimental reaction vessels were either autoclaved or rinsed with 95% ethanol. Sediments from Lake Washington were also subjected to a dose of 10^6 rads of gamma radiation from the ^{60}Co food irradiator at the College of Fisheries. In experiments using Hudson River sediments and water, all reaction vessels received additions of 0.1% (w/v) of sodium azide to inhibit any microbial populations.

3.0 RESULTS AND DISCUSSION

Three separate experiments were performed and will be discussed below.

The first experiment examined the effect of EDTA on adsorption for sediments and water samples from Cattaraugus Creek, New York. The sediment concentration was 40 mg/l. The distribution coefficients for three radionuclides--^{106}Ru, ^{137}Cs, and ^{241}Am were determined for varying concentrations of EDTA (10^{-4} to 10^{-10} M) and for a control containing no EDTA. Triplicate reaction vessels were run at the EDTA concentrations of 10^{-6} M and 10^{-10} M. Samples were collected at five time periods between 4 hours and 480 hours following the start of the experiment. For this system it appeared that K_d values for all three radionuclides achieved relatively stable values in a short time. This is shown in Table 1 where K_d values are summarized for all three radionuclides for the first and last sampling times. The data in the table imply that no significant differences existed between K_d values at the two time periods for any of the radionuclides at either concentration of EDTA (student "t" test, $\alpha = 0.05$). To evaluate the effect of EDTA, K_d values were calculated for each radionuclide over the range of EDTA concentrations. There were no apparent differences in K_d values of ^{106}Ru or ^{137}Cs for any concentration used in these experiments. However, for ^{241}Am a marked decrease in the K_d value occurred between EDTA concentrations of 10^{-4} M and 10^{-6} M. This trend is illustrated in Fig. 1, which plots K_d values of ^{241}Am against EDTA concentrations for sediment-water systems from Cattaraugus Creek.

The second experiment used sediments and water from Lake Washington with a sediment concentration of 40 mg/l. The effects of five organic compounds (acetic acid, salicylic acid, 1-nitroso-2-naphthol, 1,10-phenanthroline, and EDTA) upon K_d values for four radionuclides (^{57}Co, ^{106}Ru, ^{137}Cs, and ^{241}Am) were determined. An experimental concentration of 10^{-4} M was used for all organic compounds except 1-nitroso-2-naphthol which was run at 10^{-5} M because of its low solubility. A control containing no organic addition was also included. For the purpose of statistical analyses, triplicate experiments were run for each organic compound tested. To estimate sampling variability within a single experimental container three different samples were withdrawn from each of the three EDTA sample bottles and analyzed separately. All samples for radioactivity measurements were collected after 165 hr of shaking. The pH values in this experiment ranged from 7.05-7.55 at the beginning and from 7.9-9.1 at the end of the experiment with no apparent correlation between the different organic compounds and the change in pH values.

The results of this experiment to evaluate the effects of various organic compounds on K_d values of ^{57}Co, ^{106}Ru, ^{137}Cs, and ^{241}Am are summarized in Table 2 and in Figs. 2-5. For EDTA, the individual values in Table 2 represent only the means of triplicate measurements on individual sample bottles. In Figs. 2-5, however, the EDTA values are presented as

Table 1. Sediment-water K_d values for Cattauraugus Creek system at two different time periods and two concentrations of EDTA.

	K_d (ml/g)													
	10^{-6} M EDTA							10^{-10} M EDTA						
	$^{241}Am(x10^{-5})$		$^{106}Ru(x10^{-5})$		$^{137}Cs(x10^{-3})$			$^{241}Am(10^{-5})$		$^{106}Ru(x10^{-5})$		$^{137}Cs(x10^{-3})$		
Time (hr)	n	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	n	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
4	3	5.9	2.8	1.6	0.4	1.4	0.1	3	11.3	12.0	2.2	1.0	1.8	0.4
480	3	11.2	4.9	1.2	0.3	1.9	0.8	3	30.7	20.5	2.2	1.6	2.4	2.1

n = number of measurements
$\bar{x}$ = mean
s = one standard deviation unit

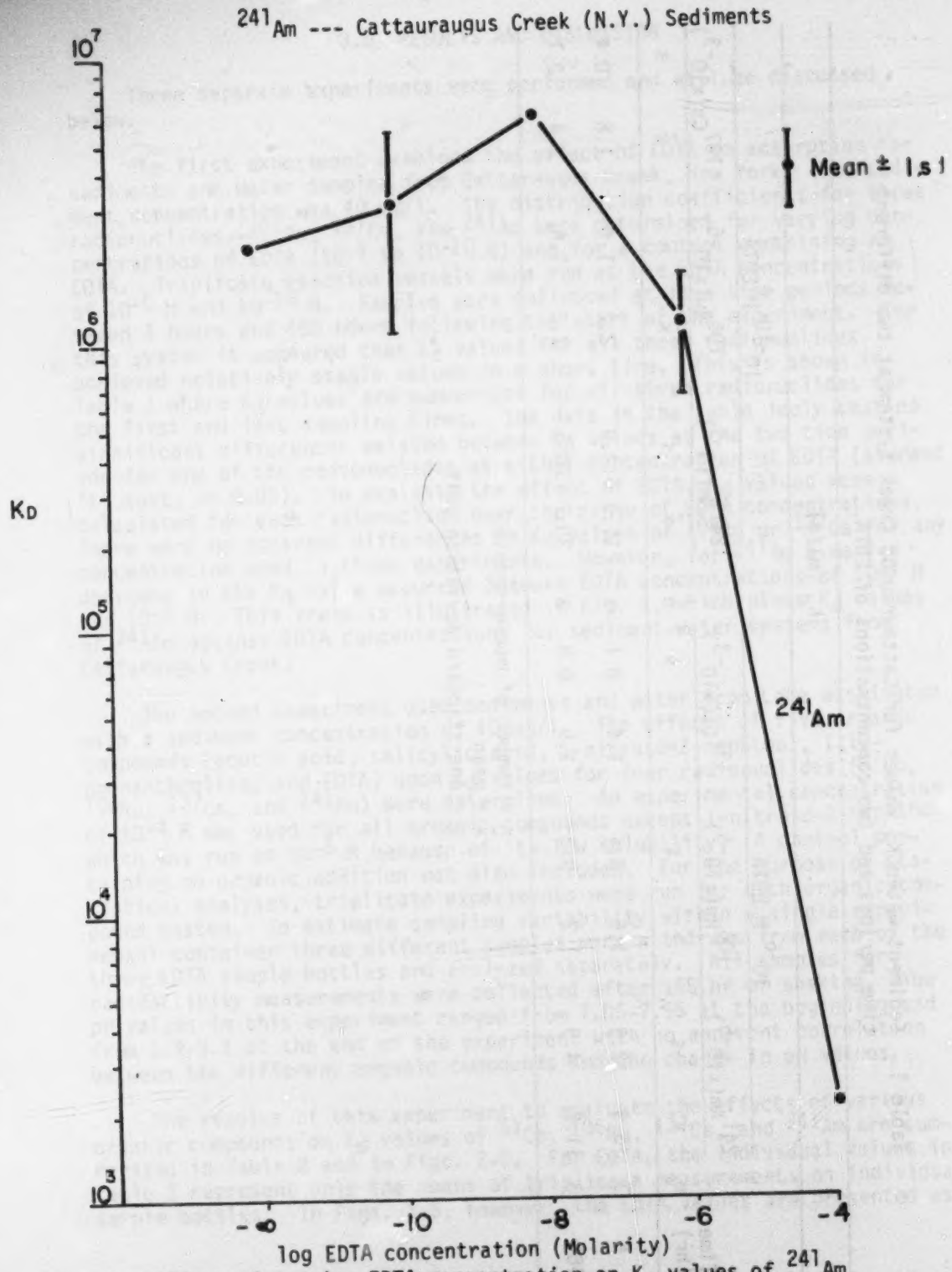

Fig. 1. Effect of varying EDTA concentration on K_d values of ^{241}Am. Values at 0 M, 10^{-8}, and 10^{-4} M EDTA are single point measurements. Values at 10^{-10} and 10^{-6} M EDTA are the mean ± one standard deviation unit for triplicate sample measurements.

Table 2. Sediment-water K_d values for Lake Washington system as a function of different organic compounds. Triplicate samples done for each organic compound (except acetic acid).

Organic compound added (concentration)	K_d			
	$^{241}Am(x10^{-4})$*	$^{57}Co(x10^{-4})$*	$^{106}Ru(x10^{-4})$*	$^{137}Cs(x10^{-2})$
None (i.e., control)	3.11 1.78 1.96	0.31 0.36 0.30	1.54 0.83 0.90	3.81 3.36 5.28
$\bar{x} \pm s$**	2.28 ± 0.71	0.32 ± 0.03	1.09 ± 0.39	4.15 ± 1.00
1-nitroso-2-naphthol (10^{-5} M)	11.24 6.07 5.98	54.41 18.31 34.73	3.79 1.99 2.04	5.83 4.71 4.57
$\bar{x} \pm s$**	7.76 ± 3.01	35.82 ± 18.07	2.61 ± 1.03	5.04 ± 0.69
1,10-phenanthroline (10^{-4} M)	23.64 28.10 24.17	20.19 12.14 18.10	3.76 3.81 3.76	3.58 2.81 3.26
$\bar{x} \pm s$**	25.30 ± 2.44	16.81 ± 4.18	3.78 ± 0.03	3.22 ± 0.39
Acetic acid (10^{-4} M)	3.88 7.32	0.42 0.48	1.70 2.89	2.15 3.24
$\bar{x} \pm s$**	5.60 ± 2.43	0.44 ± 0.04	2.30 ± 0.84	2.70 ± 0.77
Salicylic acid (10^{-4} M)	3.87 3.13 1.82	0.38 0.26 0.26	1.72 1.20 0.76	3.17 4.39 3.76
$\bar{x} \pm s$**	2.94 ± 1.04	0.30 ± 0.07	1.23 ± 0.48	3.77 ± 0.61
EDTA (10^{-4} M)	0.05 0.04 0.04	0.02 0.00 0.01	4.04 2.97 3.35	3.34 2.78 4.29
$\bar{x} \pm s$**	0.05 ± 0.01	0.01 ± 0.01	3.45 ± 0.54	3.47 ± 0.76

* significant differences between groups at $\alpha = 0.05$ level by Kruskal-Wallis statistical test.

** $\bar{x}$ and s correspond to the mean and one standard deviation unit, respectively, for the triplicate values listed.

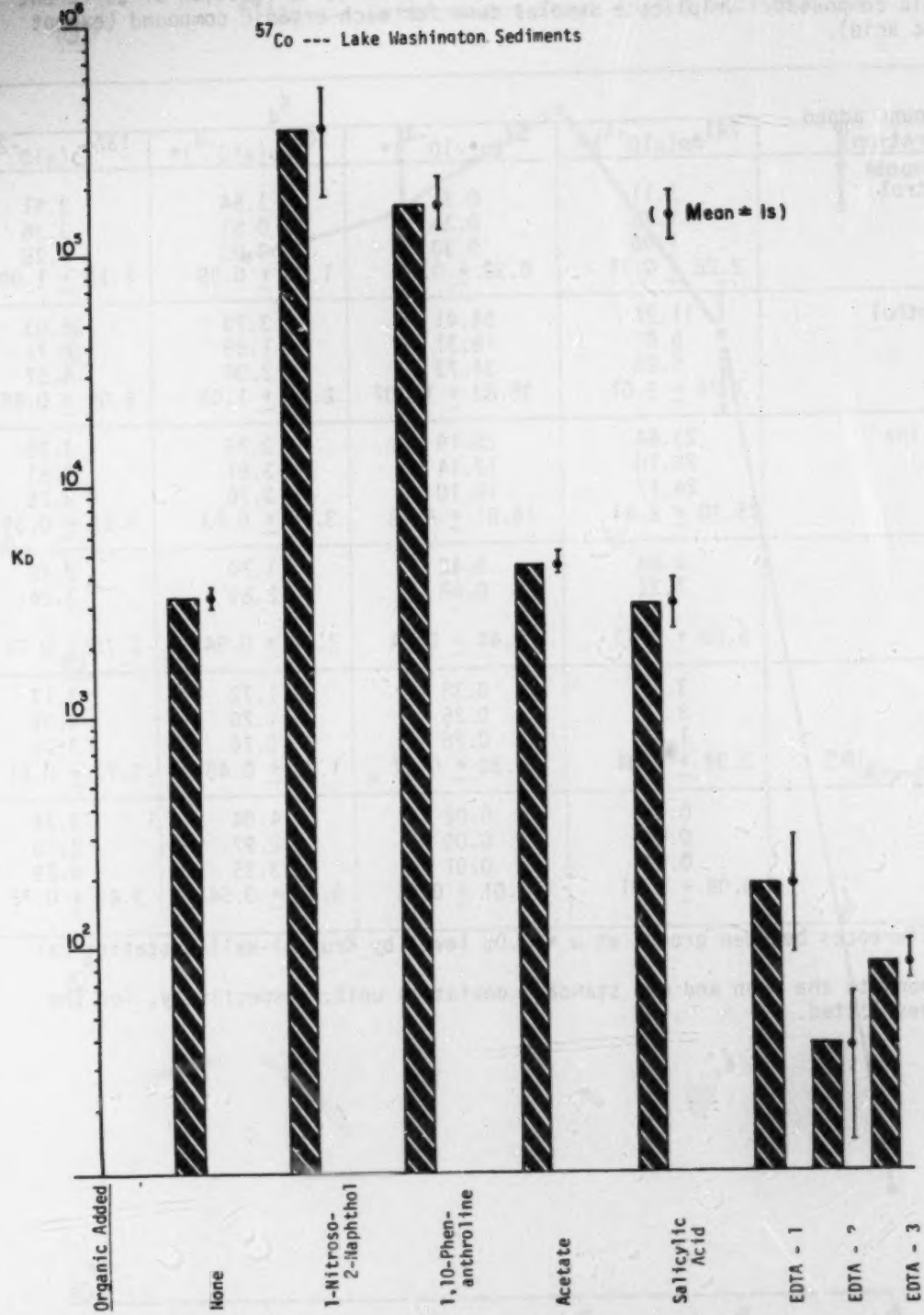

Fig. 2. Effects of organic compounds on K_d values of ^{57}Co.

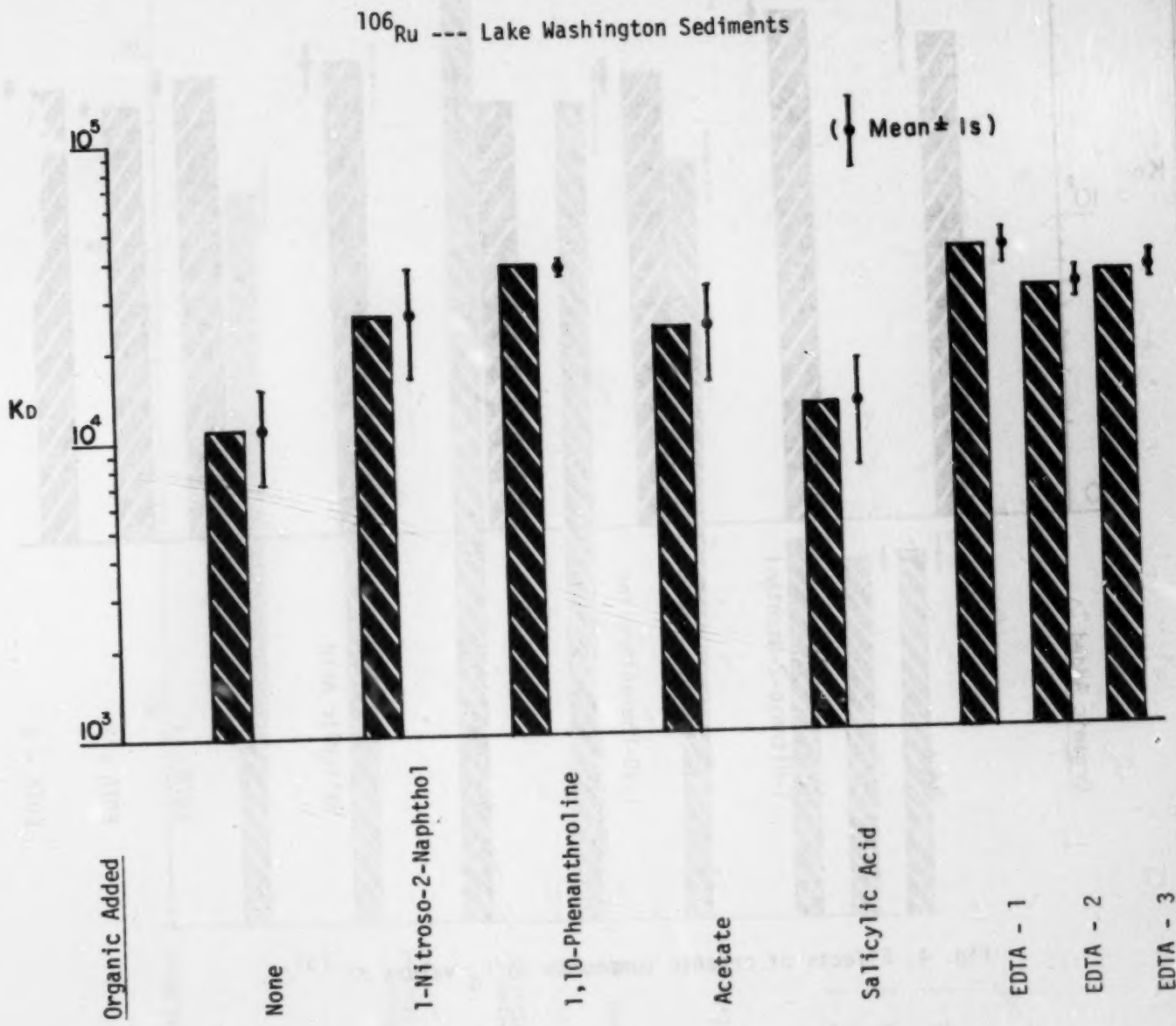

Fig. 3. Effects of organic compounds on K_d values of ^{106}Ru.

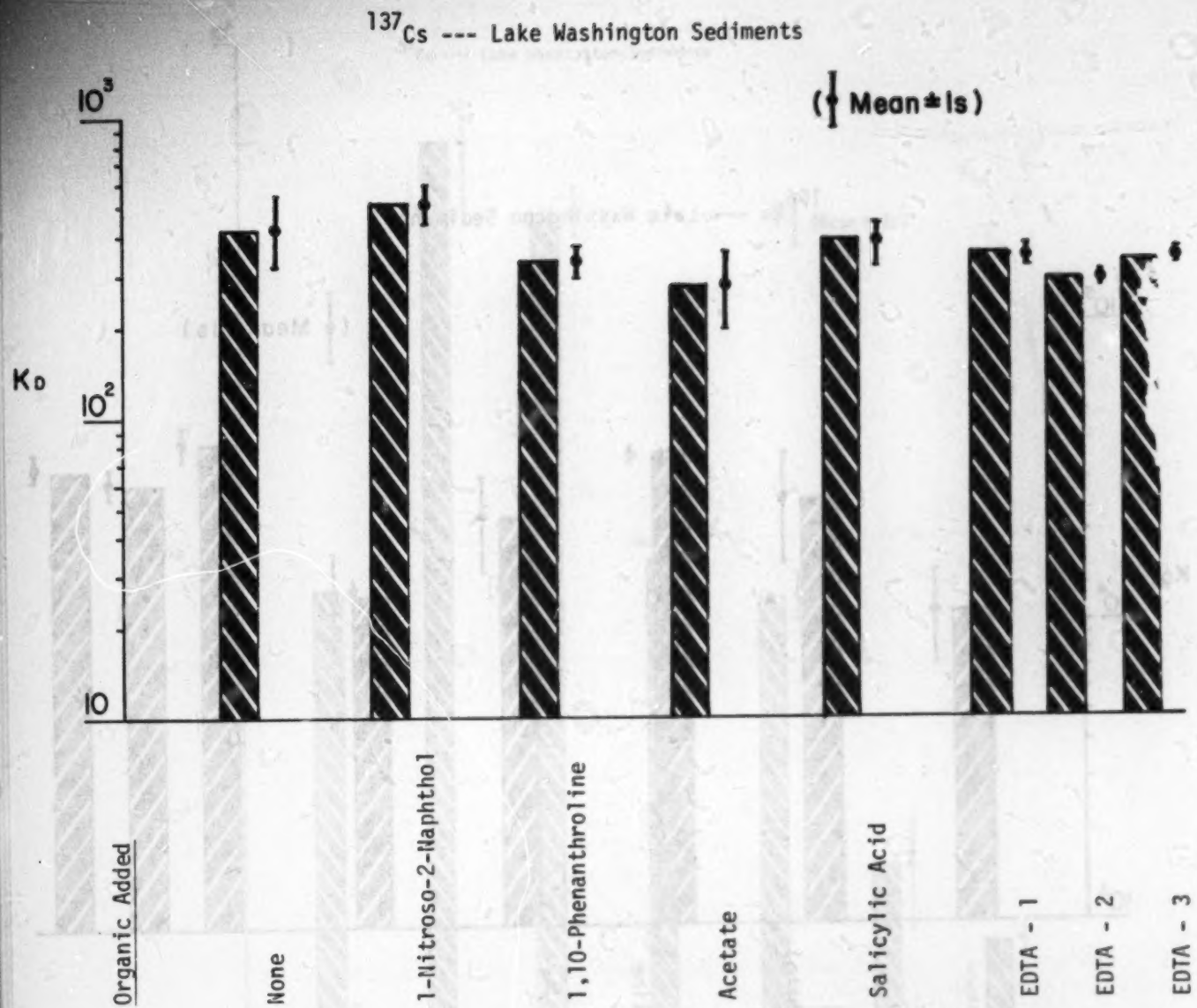

Fig. 4. Effects of organic compounds on K_d values of ^{137}Cs.

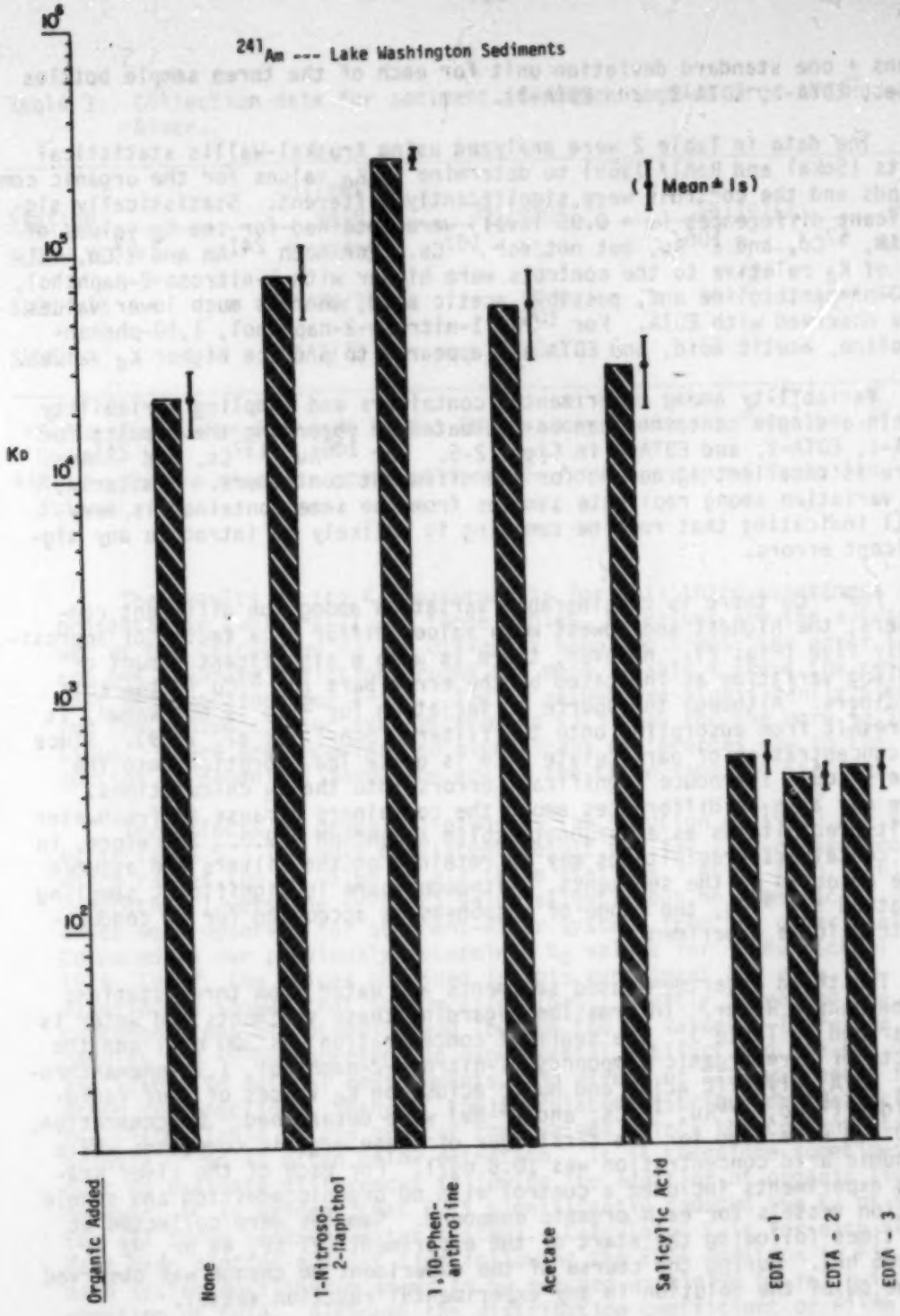

Fig. 5. Effects of organic compounds on K_d values of ^{241}Am.

means ± one standard deviation unit for each of the three sample bottles (i.e., EDTA-1, EDTA-2, and EDTA-3).

The data in Table 2 were analyzed using Kruskal-Wallis statistical tests (Sokal and Rohlf 1969) to determine if K_d values for the organic compounds and the controls were significantly different. Statistically significant differences ($\alpha = 0.05$ level) were obtained for the K_d values of ^{241}Am, ^{57}Co, and ^{106}Ru, but not for ^{137}Cs. For both ^{241}Am and ^{57}Co, values of K_d relative to the controls were higher with 1-nitroso-2-naphthol, 1,10-phenanthroline and, possibly acetic acid, whereas much lower values were observed with EDTA. For ^{106}Ru 1-nitroso-2-naphthol, 1,10-phenanthroline, acetic acid, and EDTA all appeared to produce higher K_d values.

Variability among experimental containers and sampling variability within a single container can be evaluated by observing the results for EDTA-1, EDTA-2, and EDTA-3 in Figs. 2-5. For ^{106}Ru, ^{137}Cs, and ^{241}Am there is excellent agreement for the different containers. Similarly, the variation among replicate samples from the same container is very small indicating that routine sampling is unlikely to introduce any significant errors.

For ^{57}Co there is considerable variation among the different containers; the highest and lowest mean values differ by a factor of approximately five (Fig. 2). However, there is also a significant amount of sampling variation as indicated by the error bars for ^{57}Co in the EDTA containers. Although the source of variation for ^{57}Co is not known, it may result from adsorption onto the filters (Schell et al. 1979). Since the concentration of particulate ^{57}Co is quite low, sorption onto the filters could introduce significant errors into the K_d calculations. There may also be differences among the containers because in freshwater cobalt precipitates as a carbonate solid around pH = 9.0. Therefore, in some containers precipitates may be retained on the filters and assumed to be adsorbed on the sediments. Although there is significant sampling variation for ^{57}Co, the range of responses is accounted for by conducting triplicate experiments.

The third experiment used sediments and water from three stations in the Hudson River. Information regarding these sediments and water is summarized in Table 3. The sediment concentration was 200 mg/l and the effects of five organic compounds (1-nitroso-2-naphthol, 1,10-phenanthroline, EDTA, glycolic acid, and humic acids) on K_d values of four radionuclides (^{57}Co, ^{106}Ru, ^{137}Cs, and ^{241}Am) were determined. Concentrations of 10^{-5} M were used for the first four of these organic compounds while the humic acid concentration was 10.8 mg/l. For each of the river stations experiments included a control with no organic addition and single reaction vessels for each organic compound. Samples were collected at four times following the start of the experiment (21 hr, 44 hr, 92 hr, and 165 hr). During the course of the experiment no change was observed in the pH of the solution in any experimental reaction vessel.

Table 3. Collection data for sediment and water samples from the Hudson River.

Station	Collection date	Milepost**	Salinity	pH
SLOSH VIII*	8/27/79	43.3	3.2°/oo	8.5
SLOSH IX	8/28/79	18.6	10.7°/oo	8.3
SLOSH X	9/3/79	0.1	21.0°/oo	8.2

*SLOSH stands for Standard Lamont Observatory Sediments from the Hudson.
**Mileposts are distance upstream from the southern tip of Manhattan Island.

The results of the K_d measurements for this third experiment are presented in Tables 4-7. In these tables, K_d values are the average values of the calculated K_d for different sampling times; the error terms are one standard deviation around the mean. Table 4 shows the results that were obtained for ^{137}Cs. The K_d values are significantly higher for the sediment-water systems from mp 43.3 than for the more saline stations. There are, however, no significant differences due to the introduction of organic ligands for any of the three sampling stations.

The effects of organic ligands on the sorption of ^{106}Ru are presented in Table 5. The only consistent result was for 1,10-phenanthroline which raises the K_d value at all three stations. At mp 18.6, 1-nitroso-2-naphthol lowers the ^{106}Ru K_d value slightly but no significant differences were observed for sediment-water systems from the other stations. Compared to our previously determined K_d values for ^{106}Ru (Schell et al. 1979, 1980), the values obtained in this experiment are very low. Later experiments showed that sodium azide (NaN_3) greatly increased the soluble concentrations of ruthenium and lowered the K_d values. Therefore, the results for ^{106}Ru represent an experimental artifact and are not directly applicable to natural environments. No effect of NaN_3 was noted for the other radionuclides. Many of the calculated distribution coefficients for ^{241}Am (Table 6) are greater than values, since the concentration of soluble ^{241}Am is often below detection. It is therefore sometimes difficult to evaluate differences following the addition of organic ligands. However, it is evident that EDTA significantly reduced the K_d of ^{241}Am for all three sediment-water systems. Calculated K_d's for each station have been plotted against time following the EDTA addition in Fig. 6. In each system equilibrium seems to be reached within 96 hr following the addition of EDTA. Although the distribution coefficient of ^{241}Am is reduced at all three stations, larger reductions are obtained for the

Table 4. Average K_d values for ^{137}Cs for Hudson River stations.

Organic compound	Average K_d (ml/g) for station (mean ± 1 s.d.)					
	mp 0.1		mp 18.6		mp 43.3	
	N	$K_d \times 10^{-2}$	N	$K_d \times 10^{-2}$	N	$K_d \times 10^{-2}$
None	6	6.35 ± 0.63	7	5.82 ± 0.70	6	17.4 ± 0.80
EDTA	4	6.56 ± 0.53	4	6.24 ± 0.45	4	17.7 ± 0.90
1-nitroso-2-naphthol	4	7.24 ± 0.54	4	6.03 ± 0.40	4	17.7 ± 0.50
1,10-phenanthroline	4	7.46 ± 0.56	4	6.47 ± 0.22	4	18.0 ± 0.90
Humic acid	4	7.40 ± 0.61	4	6.96 ± 0.51	4	18.5 ± 0.90
Glycolic acid	4	7.42 ± 0.49	4	6.18 ± 0.56	4	17.0 ± 0.70

N = number of sampling times after "equilibrium"

Table 5. Average K_d values for ^{106}Ru for Hudson River stations.

Organic compound	Average K_d (ml/g) for station (mean ± 1 s.d.)					
	mp 0.1		mp 18.6		mp 43.3	
	N	$K_d \times 10^{-3}$	N	$K_d \times 10^{-3}$	N	$K_d \times 10^{-3}$
None	6	4.94 ± 0.22	7	3.23 ± 0.43	6	3.22 ± 0.40
EDTA	4	5.07 ± 0.72	4	3.16 ± 0.41	4	3.15 ± 0.18
1-nitroso-2-naphthol	2	4.46 ± 0.27	2	2.52 ± 0.19	4	3.16 ± 0.27
1,10-phenanthroline	2	5.84 ± 0.29	2	3.46 ± 0.30	4	4.23 ± 0.54
Humic acid	2	5.09 ± 0.04	4	3.13 ± 0.29	4	3.52 ± 0.39
Glycolic acid	2	4.87 ± 0.16	4	3.16 ± 0.24	4	3.34 ± 0.42

N = number of data points

Table 6. Average K_d values for ^{241}Am for Hudson River stations.

Organic compound	Average K_d (ml/g) for station (mean ± 1 s.d.)					
	mp 0.1		mp 18.6		mp 43.3	
	N	$K_d \times 10^{-5}$	N	$K_d \times 10^{-5}$	N	$K_d \times 10^{-5}$
None	7	> 2.3	7	2.55 ± 0.38	7	> 2.1
EDTA	4	1.18 ± 0.48	2	0.072 ± 0.002	2	0.058 ± 0.001
1-nitroso-2-naphthol	4	> 2.5	4	> 1.9	4	> 2.1
1,10-phenanthroline	4	> 2.0	3	3.75 ± 1.25	3	2.71 ± 1.22
Humic acid	4	> 1.7	4	1.33 ± 0.24	3	0.397 ± 0.067
Glycolic acid	4	> 2.6	3	4.20 ± 0.88	3	2.65 ± 0.82

N = number of data points

Table 7. Average K_d values for ^{57}Co for Hudson River stations.

Organic compound	Average K_d (ml/g) for station (mean ± 1 s.d.)					
	mp 0.1		mp 18.6		mp 43.3	
	N	$K_d \times 10^{-2}$	N	$K_d \times 10^{-2}$	N	$K_d \times 10^{-2}$
None	7	3.63 ± 0.63	7	2.92 ± 0.62	7	9.04 ± 1.03
EDTA	4	3.21 ± 0.62	4	1.70 ± 0.29	4	3.69 ± 0.80
1-nitroso-w-naphthol	*	893 ± 391	4	5280 ± 2750	3	3510 ± 1790
1,10-phenanthroline	4	608 ± 129	4	1130 ± 110	*	668 ± 56
Humic acid	2	3.28 ± 0.12	2	3.36 ± 0.70	4	11.50 ± 0.90
Glycolic acid	2	2.75 ± 0.57	4	3.10 ± 0.45	4	9.02 ± 0.97

*K_d values did not appear to reach equilibrium after 165 hours.
N = number of data points

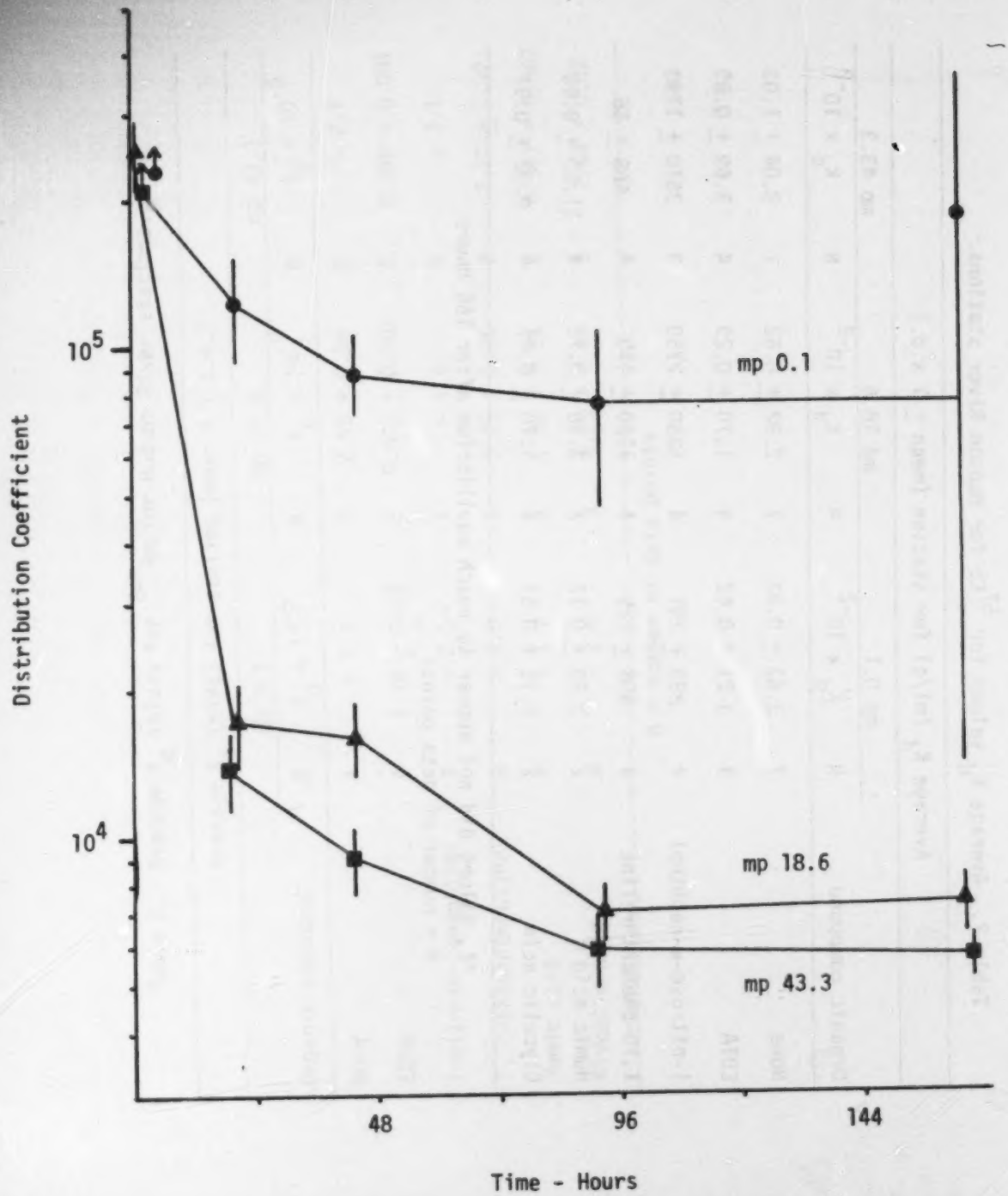

Fig. 6. Effect of EDTA on K_d values of ^{241}Am in Hudson River samples.

more freshwater stations. This occurs because EDTA chelates several di- and tri-valent cations. Since there are more metals present at the marine stations, a greater quantity of EDTA is used to complex other metals. Consequently, less EDTA is available to complex ^{241}Am in the marine sediment-water systems and the total effect is therefore reduced. The effect of other ligands on ^{241}Am K_d values can be evaluated for only the sediment-water system from mp 18.6. For that station, humic acids decrease the K_d value by approximately a factor of two while 1,10-phenanthroline and glycolic acid each increase the K_d values slightly. By evaluating the data that were collected at individual sampling times, it appears that these ligands produce similar but more pronounced responses at mp 43.3 than at mp 18.6. These effects were obscured, however, by averaging the data from different sampling times.

The most interesting results were obtained for ^{57}Co (Table 7). At mp 18.6 and mp 43.3, the addition of EDTA produces a significant decrease in the K_d value of ^{57}Co; a slight but statistically insignificant decrease was also obtained at mp 0.1. As we observed for ^{241}Am, the effect of EDTA is much more pronounced at freshwater stations. At MP 43.3, humic acids produce a slight increase in the K_d value of ^{57}Co although that effect was not observed for sediment-water systems from the other sampling stations. The most significant differences were obtained for 1-nitroso-2-naphthol and 1,10-phenanthroline. Following the addition of these ligands the distribution coefficient of ^{57}Co increased by more than two orders of magnitude for sediment-water systems from all three sampling stations. This suggests that the polycyclic ligands adsorbed strongly onto the sediment but also complexed the ^{57}Co. Although these results were quite unexpected, they indicate that the addition of some organic ligands may significantly increase the concentration of radionuclides in the particulate phase rather than increase the soluble concentration. Unlike EDTA, the effects of 1,10-phenanthroline and 1-nitroso-2-naphthol do not appear to be directly correlated with salinity. Figure 7 plots the K_d values that were obtained following the addition of 1,10-phenanthroline to sediment-water systems from each of the three sampling stations. Similar results for 1-nitroso-2-naphthol are plotted in Fig. 8. For each of these ligands a marked increase was observed 24 hr after the addition of the organic compound followed by a slight decrease at later sampling times. However, the variation with time is apparently insignificant compared to the large increase caused by the ligands.

A summary of the effects of 10^{-4}-10^{-5} M concentrations of the organic compounds on all samples tested is presented in Table 8.

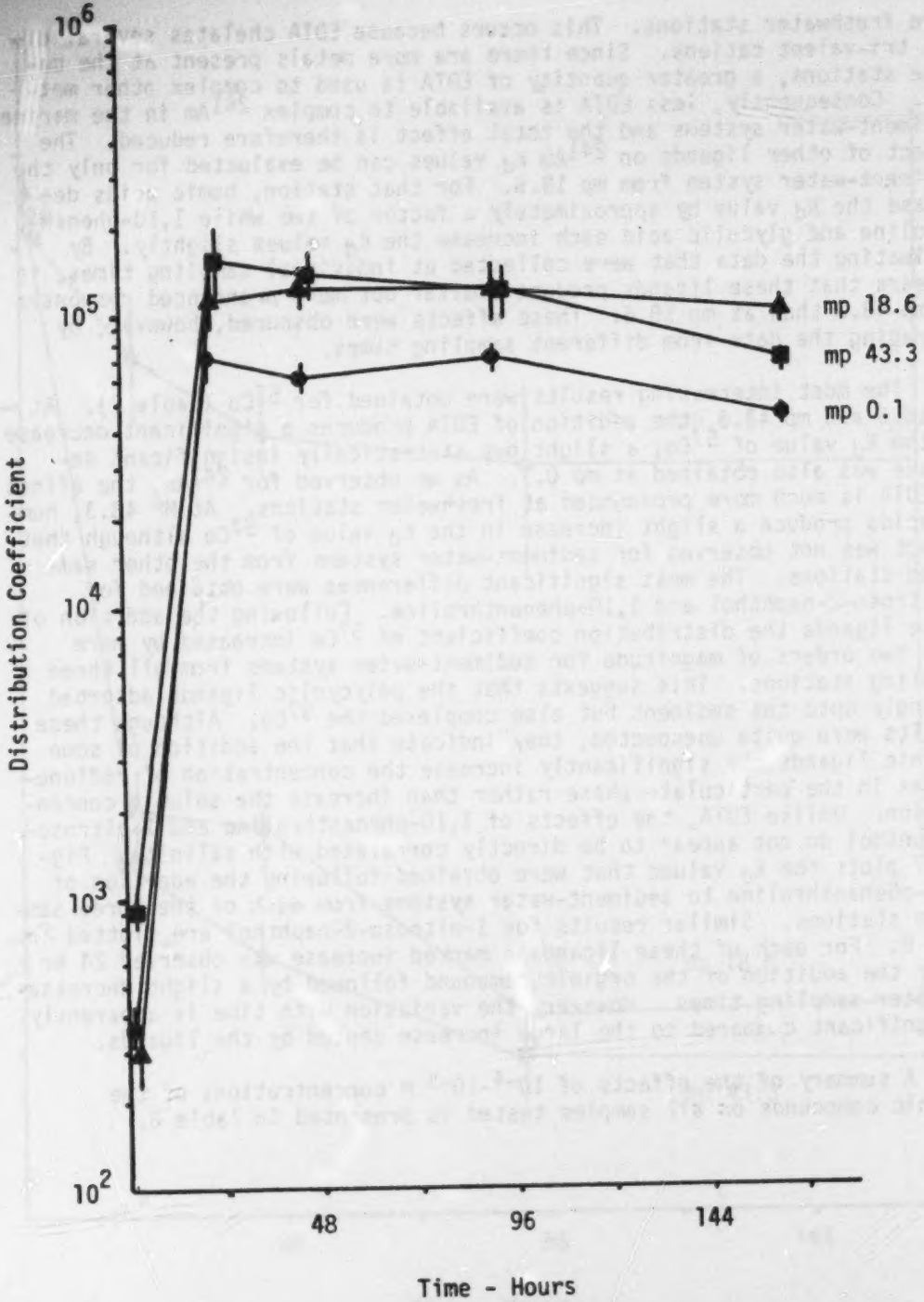

Fig. 7. Effect of 1,10-phenanthroline on K_d values of ^{57}Co in Hudson River samples.

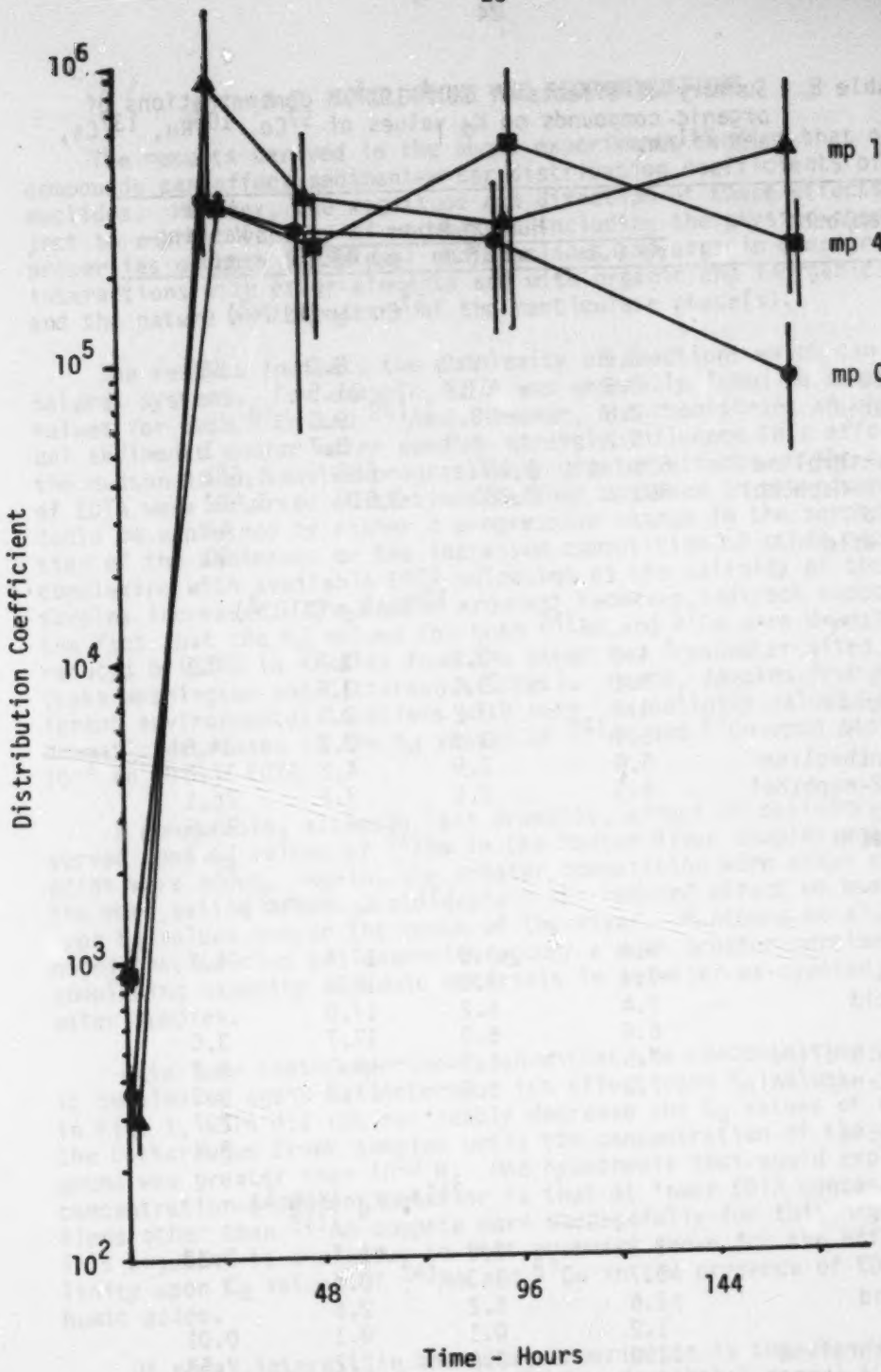

Fig. 8. Effects of 1-nitroso-2-naphthol on K_d values of ^{57}Co in Hudson River samples.

Table 8. Summary of effects of 10^{-4}-10^{-5} M concentrations of organic compounds on K_d values of ^{57}Co, ^{106}Ru, ^{137}Cs, and ^{241}Am.

Organic compound added	Hudson River mp 0.1	Hudson River mp 18.6	Hudson River mp 43.3	Lake Washington
		^{57}Co K_d ($X10^{-2}$)		
None	3.6	2.9	9.0	32
Humic acids	3.3	3.4	11.5	
Glycolic acid	2.8	3.1	9.0	
EDTA	3.2	1.7	3.7	1
1,10-phenanthroline	608	1,130	668	1,681
1-nitroso-2-naphthol	893	5,280	3,510	3,582
Acetic acid				44
Salicylic acid				30
		^{106}Ru K_d ($X10^{-3}$)		
None	4.9	3.2	3.2	10.9
Humic acids	5.1	3.1	3.5	
Glycolic acid	4.9	3.2	3.3	
EDTA	5.1	3.2	3.2	34.5
1,10-phenanthroline	5.8	3.5	4.2	37.8
1-nitroso-2-naphthol	4.5	2.5	3.2	26.1
Acetic acid				23.0
Salicylic acid				12.3
		^{137}Cs K_d ($X10^{-2}$)		
None	6.4	5.8	17.4	4.2
Humic acids	7.4	7.0	18.5	
Glycolic acid	7.4	6.2	17.0	
EDTA	6.6	6.2	17.7	3.5
1,10-phenanthroline	7.5	6.5	18.0	3.2
1-nitroso-2-naphthol	7.2	6.0	17.7	5.0
Acetic acid				2.7
Salicylic acid				3.8
		^{241}Am K_d ($X10^{-5}$)		
None	>2.3	2.6	>2.1	0.23
Humic acids	>1.7	1.3	0.4	
Glycolic acid	>2.6	4.2	2.6	
EDTA	1.2	0.1	0.1	0.01
1,10-phenanthroline	>2.0	3.8	2.7	2.53
1-nitroso-2-naphthol	>2.5	>1.9	>2.1	0.78
Acetic acid				0.56
Salicylic acid				0.29

4.0 CONCLUSIONS AND RECOMMENDATIONS

The results derived in the above experiments confirm that organic compounds can affect sediment-water distribution coefficients of radionuclides. However, the magnitude and direction of these effects are subject to a great variety of parameters including the physico-chemical properties of both individual radionuclides and organic compounds, their interactions with other elements and with organic and inorganic compounds, and the nature and chemistry of the particulate phase(s).

The results indicate the complexity of reactions which can occur in natural systems. For example, EDTA was generally found to lower the K_d values for both ^{57}Co and ^{241}Am. However, the chemistries of the individual sediments and/or water samples strongly influence this effect. In the Hudson River samples progressively greater effects on the K_d values of EDTA were observed at stations farther upstream in the river. This could be explained by either a progressive change in the sorption properties of the sediments or the increased competition of other cations for complexing with available EDTA molecules as the salinity of the water samples increased. The latter argument receives indirect support from the fact that the K_d values for both ^{241}Am and ^{57}Co were dramatically reduced by EDTA in samples from the other two freshwater sites tested (Lake Washington and Cattaraugus Creek). Hence, samples from three different environmental locations with very low salinity values showed dramatic decreases in the K_d values of ^{241}Am and ^{57}Co upon addition of 10^{-4} to 10^{-5} M EDTA.

A comparable, although less dramatic, effect of salinity was observed upon K_d values of ^{241}Am in the Hudson River samples when humic acids were added. Again, the greater competition with other cations in the more saline waters could explain the reduced effect of humic acids upon K_d values nearer the mouth of the river. Mantoura et al. (1978) noted that calcium and magnesium occupy a much greater portion of the complexing capacity of humic materials in seawater as opposed to freshwater samples.

Data from these experiments show that the concentration of an organic complexing agent can determine its effect upon K_d values. As shown in Fig. 1, EDTA did not noticeably decrease the K_d values of ^{241}Am in the Cattaraugus Creek samples until the concentration of the organic compound was greater than 10^{-6} M. One hypothesis that could explain this concentration-dependent behavior is that at lower EDTA concentrations, cations other than ^{241}Am compete more successfully for this organic ligand. This argument is analagous to that proposed above for the effect of salinity upon K_d values of ^{241}Am and ^{57}Co in the presence of EDTA and humic acids.

Of equal interest in the above experiments is the observation that certain organic ligands (e.g., 1-nitroso-2-naphthol, and 1,10-phenanthroline) can increase the affinity of certain radionuclides for the

particulate phase. This implies that such organic ligands are involved in a dual reaction process: 1) they are complexing the radionuclide, and 2) they are themselves actively associating with the sediment particles. Similar phenomena have been observed by Davis and Leckie (1978a and b) for trace metal-organic combinations. Depending upon the relative affinities of ligands for the radionuclide and the sediment particles, lowering the concentration of the ligand could result in lower K_d values than in the control (i.e., no ligand added).

Our results identify processes which are occurring in natural systems and suggest several interesting and important directions for further study. These results emphasize the complex variety of interacting factors that can affect sediment-water distributions of radionuclides. Therefore, it is necessary in any adsorption study, whether in the laboratory or in the field, to characterize as fully as possible the chemical parameters of water and sediment that can contribute to the eventual results in any given system. Our results provide a starting point for information regarding the effect of organic compounds upon the environmental fate and distribution of radionuclides. However, the environmental relevance of many of these test compounds has not been determined. Consequently, further studies should make an attempt to use "natural" compounds. Humic acids are certainly environmentally relevant and should be pursued in much greater detail. This could include not only obtaining humic materials from different environmental sources but also fractionating a humic sample into various components. For example, Rashid (1971) has shown that different molecular weight size fractions of humic substances have different metal complexing efficiencies. The use of "biologically conditioned" water samples for K_d studies could also be particularly interesting. Such a water sample could be obtained by allowing biota to grow in it prior to use for K_d studies. It is clear that much research remains to be done in this interesting and complicated area before we can hope to understand the environmental behavior of anthropogenic radionuclides.

5.0 SUMMARY - EFFECTS OF ORGANIC COMPOUNDS

Results of the studies on the effects of organic compounds show that certain organic compounds can definitely affect sediment-water K_d values. For example, EDTA and humic acids can solubilize both ^{241}Am and ^{57}Co, although this effect is more pronounced in freshwater than in seawater sediment-water systems. Other organic compounds such as 1-nitroso-2-naphthol and 1,10-phenanthroline actually increase the affinity of radionuclides such as ^{241}Am and ^{57}Co for sediments. However, certain radionuclides such as ^{137}Cs and ^{106}Ru showed little or no alteration in their interactions with natural sediments due to any of the organic compounds tested. To conclude, organic compounds can affect the eventual distribution and fate of radionuclides in natural water systems, but our ability to predict such interactions requires a knowledge of the physical and chemical properties of: 1) the given radionuclide, 2) the important organic ligands, 3) the solid phases present, and 4) the receiving waters. Although this preliminary research has produced valuable and interesting results, much more research is necessary before we can hope to understand the role of organic compounds in mobilizing anthropogenic radionuclides.

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Organic compounds have the capacity to alter the partitioning between particulate and soluble phases of certain radionuclides in sediment-water systems from natural environments. We studied the effects of a variety of selected organic compounds upon sediment-water distribution coefficients for four radionuclides--^{57}Co, ^{106}Ru, ^{137}Cs, and ^{241}Am. Natural sediment-water samples from lake, river, and estuarine environments were used in these studies. The results show that organic compounds can significantly change the distributions of some radionuclides between water and sediment, although other environmental factors must be considered in association with the organic compounds.

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